Raman study of ionic water-based copper and zinc ferrite magnetic fluids

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Abstract

Raman spectroscopy is used to investigate the OH-bending and OH-stretching modes of chemisorbed OH-groups in copper-ferrite and zinc-ferrite water-based magnetic fluid samples. Room-temperature Raman spectra were taken from diluted magnetic fluid samples and compared with the spectrum taken from liquid water. The suppression of the symmetric OH-stretching Raman modes from the ionic magnetic fluid sample spectra is discussed in terms of the replacement of a hydrogen atom from the water molecule by the nanoparticle surface. Moreover, changes on the area ratio between hydrogen bonded and nonhydrogen bonded OH-Raman peaks in the ionic magnetic fluid samples, as compared to the OH-Raman peaks from liquid water, are discussed in terms of changes on the hydrogen bond strength. © 1999 Elsevier Science B.V. All rights reserved.

Magnetic fluids are ultra-stable colloidal systems consisting of monodomain magnetic nanoparticles dispersed in organic or inorganic liquid carrier. The stability of magnetic fluids is achieved through the balance between opposite particle interaction tendencies. From one side, particle thermal motion and particle–particle repulsion work together to keep particles apart. From the other side, Van der Waals and magnetic dipole interaction tend to stick particles together. Different repulsion mechanisms are used to prevent particle–particle clustering, thus responding for different types of magnetic fluids. Steric repulsion prevents agglomeration in surfaced magnetic fluids, whereas coulombic repulsion accounts for stability in ionic magnetic fluids [1]. High resolution microscopy, X-ray diffraction, magnetization measurements and optical birefringence measurements are the magnetic fluid standard characterization techniques [2]. Magnetic resonance has also been used as a technique to characterize [3,12] as well as to study [4,13,14] many of the properties of magnetic fluids. However, the complexity of the magnetic fluid system and the increasing interest for new applications require more detailed investigation of their properties. In particular, the physico-chemical nature and properties of the molecular layer chemisorbed at the nanoparticle surface plays a central role on the

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stability of magnetic fluids, though little effort has been done to investigate the structure and the interaction of the chemisorbed layer with the surrounding medium. Raman spectroscopy is probably the most important experimental technique available to obtain information concerning the intra- and inter-molecular vibrational modes of liquid water [5], though it never has been used to investigate water-based magnetic fluids. The Raman spectra of aqueous-based systems are dominated by hydrogen bonding as well as by nonhydrogen bonding, thus being a suitable experimental technique to investigate details of the water-based layer about the magnetic nanoparticle. The intermolecular restricted translational modes and librational modes associated to liquid water occur respectively below 200 cm^{-1} and between 300 and 1000 cm^{-1}, at room temperature and ambient pressure [6]. The two intra-molecular OH-bending modes for liquid water occur around 1600 cm^{-1} [7]. The higher frequency OH-bending mode (v_2') is associated to nonhydrogen bonded water, whereas the lower frequency OH-bending mode (v_2) is associated to hydrogen bonded water. The five intramolecular OH-stretching modes in liquid water, however, occur from 2800 to 4000 cm^{-1} and arise from the various amounts of hydrogen bonding within the framework of a tetrahedral bonded structure [8]. The two OH-stretching Raman components at the higher end frequency of the spectra describe nonhydrogen bonded modes (v^s and v^a) of liquid water, whereas the three Raman components at lower frequencies describe hydrogen bonded modes (v_d^s, v_d^a and v_b) of liquid water. In this work Raman spectroscopy is used to investigate the water-based interface nanoparticle surface-carrier liquid in ionic magnetic fluids. The room-temperature Raman spectra obtained from the recently synthesized copper and zinc ferrite-based ionic magnetic fluids will be presented and discussed.

The chemical synthesis of high-quality $CuFe_2O_4$ and $ZnFe_2O_4$ based ionic magnetic fluid samples have been obtained only recently [9]. The samples used in our experiment were prepared using the condensation method by coprecipitating aqueous solution of copper, zinc and iron salts in alkaline medium, followed by peptization of the fine particles in water. The mean particle diameter (particle

dispersion) of the copper and zinc samples, respectively on the order of 9.8 nm (0.2) and 14.3 nm (0.2), were estimated from X-ray measurements [9]. The saturation magnetization was obtained from a vibrating sample magnetometer and for the zinc sample is on the order of 1.4 emu/g at 200 K [10]. The saturation magnetization of the copper sample has not been determined. Double distilled water and diluted (0.1 molar concentration) copper and zinc ionic magnetic fluid samples were used to obtain the Raman spectra at room temperature. The experimental setup composed of a double 0.85 m 1401 Spex monochromator equipped with a water-cooled Gallium Arsenide Hamamatsu photomultiplier tube and a SR400 model photocounter was used to take the Raman spectra. The samples were optically excited with the 488.0 nm line from an argon ion laser at an optical power on the order of 150 mW outside the sample holder. The Raman spectra in the typical intra-molecular OH-bending and OH-stretching mode regions taken from liquid water, diluted copper and diluted zinc ionic magnetic fluid samples are shown respectively in Fig. 1 (full circles) and Fig. 2 (full squares). Solid lines in Fig. 1 represent the best fitting of the Raman spectra of liquid water, diluted copper and diluted zinc ionic magnetic fluid samples corresponding to the intra-molecular OH-bending modes, using Gaussian-shaped curves. Dashed lines in Fig. 1 represent the individual OH-bending modes according to our fitting procedure. Likewise, the solid lines in Fig. 2 represent the best fitting of the Raman spectra of liquid water, diluted copper and diluted zinc ionic magnetic fluid samples corresponding to the intra-molecular OH-stretching modes, using Gaussian-shaped curves. The fitted OH-stretching modes are shown separately as dashed lines in Fig. 2. The hydrogen bonded OH-bending (v_2), nonhydrogen bonded OH-bending (v_2'), symmetric hydrogen bonded OH-stretching (v_d^s), asymmetric hydrogen bonded OH-stretching (v_d^a), asymmetric partially bonded OH-stretching (v_b), symmetric nonhydrogen bonded (v^s) and asymmetric nonhydrogen bonded (v^a) Raman shifts were identified from the data available in Ref. [8] and are shown in Table 1.

We first discuss the most striking result we found from our data (see Table 1), namely, the
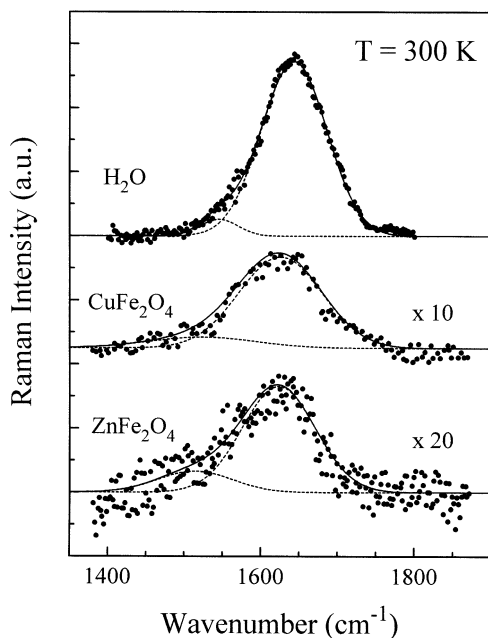
Fig. 1. Full circles represent the Raman spectra in the OH-bending region whereas the solid lines represent the best fitting using gaussian-shaped curves. Dashed lines represent the deconvoluted OH-bending modes.
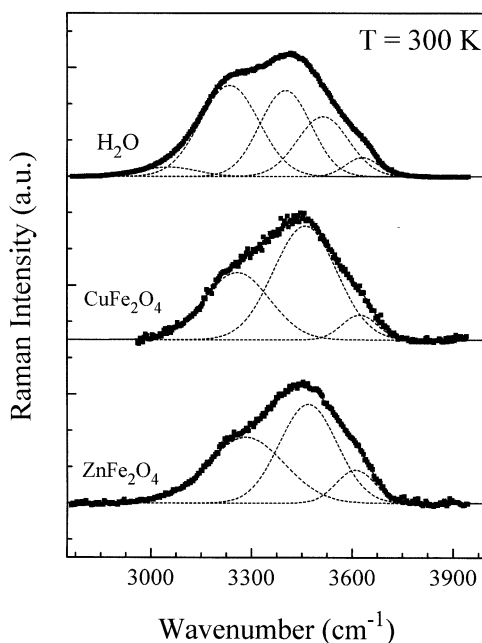

Fig. 2. Full squares represent the Raman spectra in the OH-stretching region whereas the solid lines represent the best fitting using gaussian-shaped curves. Dashed lines represent the deconvoluted OH-stretching modes.

suppression of all symmetric OH-stretching modes from the magnetic fluid Raman data. This observation is supported by the fitting of the OH-stretching band in ionic magnetic fluids with three Raman peaks instead of five Raman peaks as in pure water. Though in pure water the OH-stretching mode at 3051 cm^{-1} is just a shoulder, the OH-stretching mode at 3511 cm^{-1} is a quite intense peak. Thus, the suppression of the higher frequency symmetric OH-stretching mode from the ionic magnetic fluid

Raman spectra is easily detected by any robust fitting procedure. This is a strong evidence that the Raman spectra from the ionic magnetic fluid samples are dominated by the hydroxyl-groups chemiosorbed at the nanoparticle surface. Stabilization of metal-oxide solid surfaces in contact with aqueous media, involving chemisorption of OH-groups at the metal-ion sites, is well known. Further, the high band gap semiconductor magnetic nanoparticles dispersed in the dielectric carrier

Table 1
Liquid water, copper and zinc ferrite-based ionic magnetic fluid OH-bending and OH-stretching Raman modes at ambient temperature and ambient pressure, and hydrogen bond strength values

Sample	Bending (cm^{-1})		Stretching (cm^{-1})					ΔH (kcal/mol)
	v_2	v_2'	v_d^s	v_d^a	v_b	v^s	v^a	
Water	1545	1643	3051	3233	3399	3511	3628	2.74
$CuFe_2O_4$	1524	1625	–	3257	3458	–	3620	3.66
$ZnFe_2O_4$	1514	1624	–	3260	3470	–	3621	3.87

liquid work as a highly efficient scattering centers for visible light. Therefore, water-molecules themselves, either close to or far away from the magnetic surface particle, do not scatter as much the incident laser line as the chemisorbed hydroxyl-group at the nanoparticle surface. Accordingly, suppression of all symmetric OH-stretching Raman modes from the ionic magnetic fluid sample data is an obvious consequence of the vibrational quenching effect due to the replacement of a hydrogen atom from water by the magnetic nanoparticle surface. Secondly, from the Raman OH-stretching data we estimated the hydrogen bond strength or the enthalpy change (ΔH) in liquid water and in ionic magnetic fluid, using the van't Hoff equation [11,15]. In fact, to the liquid water equilibrium (O—H•••O⇌O—H + O) it has been assigned an enthalpy on the order of $\Delta H = 2.53$ kcal/mol [5]. The liquid water equilibrium constant (K) has been calculated as the ratio A_B/A_U, where A_B is the sum of the integrated Gaussian Raman components related to the hydrogen bonded OH-stretching modes and A_U is the sum of the integrated Gaussian Raman components related to the nonhydrogen bonded OH-stretching modes. The van't Hoff equation reads $\ln K = A - \Delta H/RT$, where $R = 1.99$ cal/mol $\times$ K is the gas constant, T is the absolute temperature and $A = -3.579$ is the intercept constant for liquid water [5]. Assuming the intercept constant for chemiosorbed OH-groups in water-based liquid systems equals to -3.579, the hydrogen bond strength was estimated from the Raman data at room-temperature, as shown in the last column of Table 1. The enthalpy change we found for liquid water ($\Delta H = 2.74$ kcal/mol) is in very good agreement with the literature. This is a strong indication of the robustness of our fitting procedure. The enthalpy change we found for the ionic magnetic fluid samples, however, is dramatically enhanced with respect to the value we found for liquid water. As shown in Table 1 the enthalpy change increases, with respect to liquid water, by an amount on the order of 34 and 41% for copper and zinc ferrite-based ionic magnetic fluids, respectively. Moreover, the hydrogen bonded OH-bending mode (v_2) in the Raman spectra of ionic magnetic fluids show a huge increase in its relative area, going from 5% for liquid water up to 14 and 17% for copper and

zinc ferrite-based magnetic fluids, respectively. Both results are strong indication that the chemisorbed OH-groups are firmly bonded to the first water layer about the magnetic nanoparticle surface. Small Raman shifts observed on the remaining OH-bending and OH-stretching modes in the magnetic fluids are influenced by the quenching effect as mentioned above as well as by the differences on the surface-atom sites (Zn^{2+}, Cu^{2+}, Fe^{3+}) where the OH-groups are chemisorbed. A quantitative discussion involving the main features as well as the details of the above mentioned Raman results, including new data taken from maghemite, nickel, manganese and cobalt ferrite-based ionic magnetic fluids, are presently in progress and will be delivered in a forthcoming publication.

In conclusion, the usefulness of the Raman spectroscopy in the study of magnetic fluids is first demonstrated in this work. In particular, Raman spectroscopy would be used as a powerful technique to investigate the microscopic details of the first molecular layers about the nanoparticle surface, i.e., the interface nanoparticle surface-carrier liquid. Suppression of the symmetric OH-stretching modes from the Raman spectra is a strong indication that chemisorbed OH-groups dominate the light scattering process in ionic magnetic fluid samples. In addition, a huge increase on the hydrogen bond strength about the nanoparticle surface is indicated through the evaluation of the area ratio of the hydrogen to the nonhydrogen OH-stretching modes as well as through the enhancement of the hydrogen bonded OH-bending Raman mode signal as compared to the nonhydrogen OH-bending one.

Acknowledgements

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